THE COMPARATIVE INFLUENCE OF SHORT AND LONG RANGE CRYSTALLINE ELECTRIC FIELDS ON THE MAGNETIC BEHAVIOUR OF THE PARAMAGNETIC SALTS OF THE IRON GROUP OF ELEMENTS

PART II

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ABSTRACT. In the first half of the iron group of elements between Ti^{+++} to Fe^{+++}, the orbital contributions to the magnetic moments are small or totally absent and the salts should approximately obey the Curie law. Effect of the long range fields, therefore, would be difficult to detect. When, however, a close investigation is made it is found that the moment-temperature curves even for these ions deviate from salt to salt, and from the Curie law appreciably, indicating the action of long range fields, as also the effect of the higher order terms usually neglected in discussions. The scope of the Jahn-Teller theorem, picturising the inherent mechanism for removal of degeneracy of the paramagnetic ion, is discussed and extended to the whole of the crystal lattice. It is pointed out that when so extended the Jahn-Teller mechanism is identified with the entire crystalline field effect, and no extra mechanism is necessary to explain the effect of the distant atoms on the paramagnetic ion.

1. INTRODUCTION

It is now well known that the magnetic behaviour of the paramagnetic ions in their solid salts and solutions may be explained to considerably minute details, on the basis of the existence in them, of strong and asymmetric electric fields, arising out of clusters of diamagnetic ions and dipoles, immediately surrounding the paramagnetic ions. The existence of such closely bonded asymmetric clusters is directly verified by the X-ray data on the fine structure of these salts in addition to other indirect methods such as absorption spectra, magnetic birefringence, etc. Especially, in the iron group of salts, such data, in a large majority of cases, point to an octahedral coordination of the paramagnetic ions, though other structures such as tetrahedral, square, etc., do also sometimes occur.

The effect of such electric fields in the paramagnetic salts is to split up the magnetically degenerate ground state of the paramagnetic ions into Stark-patterns. For the ionic salts of the iron group of elements, the fields are just sufficient to break down the L.S coupling and then the symmetric or

cubic part of the field partially removes the orbital degeneracy, thus quenching more or less the orbital contributions to the effective moments, whereas, the asymmetric (or rhombic) part removes the remaining orbital degeneracy, as also to some extent the spin degeneracy. The cubic and the rhombic splittings at ordinary temperatures are of the order of $h\Delta\nu_{\text{Cubic}} > kT$, and $h\Delta\nu_{\text{Rhombic}} \sim kT$ for the orbital parts and $h\Delta\nu_{\text{Rhombic}} < kT$ for the spins. For both the F- and the D-state ions, containing x and $5+x$ electrons in the $3d$ subshell, when the coefficient of the cubic part of the electric field has a positive sign, as happens with an octahedral coordination of the paramagnetic ion, triply degenerate orbital levels lie lowest in the Stark-pattern ; whereas, with $5-x$ and $10-x$ electrons a singlet is the lowest for the F-state and a doublet for the D-state. On the other hand, with a negative sign of the cubic field constant, as occurs with a tetrahedral coordination, the entire position is exactly reversed. It is very satisfactory that with highly hydrated ionic salts of the iron group, in which complications due to exchange forces, magnetic dipole-dipole interactions and strong covalent forces do not arise, the predictions of the above simple theory for the magnetic behaviours are surprisingly well fulfilled*.

It is interesting to note that the necessity of postulating a mechanism such as above, for anisotropically quenching the magnetic moments of the paramagnetic ions in solid salts and solutions, follows as a natural consequence of the well known principle enunciated by Jahn and Teller (1937, 1938), which tells us that the underlying degeneracy of the ground state of the paramagnetic ion, associating with a closly bound cluster of other atoms, causes a distortion of the cluster such that the resulting asymmetry in the electric field due to the cluster is sufficient to remove the said degeneracy, consistent with the conditions of stability of the system. It is, however, to be remembered that during the formation of the lattice structure in crystalline substances, forces other than those arising from the members of the closest bound ionic clusters are brought to play upon the paramagnetic ion. Though the direct actions of such distant atoms may not be, in general, of much importance, their indirect influence by distorting the nearest cluster even slightly (of the order of about 10^{-9} cm., Van Vleck, 1939) may be quite large, of the same order as the primary Jahn-Teller effect.

Theoretically, perhaps, we should not differentiate between the Jahn-Teller effect and the action of the distant atoms. For the Jahn-Teller effect need not confine itself to the nearest cluster alone, and also it is very probable that the distortions in the arrangements of the distant atoms and the consequent induced asymmetry in the nearest cluster are ultimately to a large extent the repercussions of the primary Jahn-Teller effect. Experimentally, however, it should be possible to distinguish between these two effects and to compare their magnitudes.

* For full reference see Part I of the present paper

For example, if some, at least, of the asymmetry of the nearest ionic clusters in the solid salts were due to this distorting action of the distant atoms, then in the state of solution, where the distant atoms have on the average a spherical symmetry, and in any case are too far out to produce appreciable effect, we should observe a fairly large departure in the magnetic behaviour from the solid state. Further, in a series of salts of a given paramagnetic ion having the same ionic cluster but different distant atoms in the unit cell, we should observe small but appreciable differences in the effective magetic moments (Bose 1948 ; Bose and Mitra 1952).

In view of the above, it has become necessary to examine afresh the available magnetic data on suitable salts and solutions of the iron group. Out of the vast array of rather haphazard experimental data, which are found in the literature, and from which at first sight it appears well nigh impossible to throw any light on the present problem, we have been able to gather the following informations for details of which reference may be made to the earlier part of this paper (*l.c.*)

(1) The values of the mean effective moments for the different salts and their solutions at room temperatures, of a given paramagnetic ion, are apparently remarkably constant for many of the iron group elements, which is not surprising since, in many of these the orbital moments are more or less completely quenched, by the electric fields and only the spins, very little so affected, remain.

(2) On a closer observation, however, a few cases will be found, in which orbital contributions are not so effectively quenched, showing, indeed, appreciable differences of the effective moments from salt to salt and from solid to solution and seeming to point to the existence of some effect of the long range fields, though not as much as predicted by a recent theory of Van Vleck (1939) and demanded by the paramagnetic absorption and resonance experiments*.

It has been suggested in the earlier paper (*l.c*) that the mean effective moments of the salts at room temperatures are not probably sufficiently sensitive to the changes in the long range fields, so as to make the consequent changes in the mean moments felt, over the rather large exprimental uncertainties. It is, however, probable that, even allowing for the experimental errors, in many cases, it might be necessary to invoke some other mechanism which masks the rather large effect of the distance atoms postulated by Van Vleck and others (*loc. cit.*).

In the present paper we shall analyse the existing experimental results on the variations with temperature of the mean effective moments of the salts of the iron group of elements, with a view to clarifying the present unsatisfactory state of our knowledge regarding long range electric fields acting on the paramagnetic ions.

* For a brief review of these results reference may be made to the masterly lecture by Van Vleck published in Amer. Jour. Phys. 1950.

2. THE SCOPE OF THE JAHN-TELLER MECHANISM IN QUENCHING THE ORBITAL MOMENTS OF THE PARAMAGNETIC IONS

From the discussions of the conditions of stability of paramagnetic ionic clusters as given by Jahn and Teller (1937, 1938) and Van Vleck (1939), it appears that in such a magnetically degenerate system, the symmetrical modes of vibrational displacements will be equivalent to several such nearly instantaneous distortional configurations of the cluster, amongst which the system will resonate, provided that the time average over the various configurations is consistent with the minimum symmetry requirements of the space group, which will amount to a coupling between the different members of the cluster sufficiently asymmetric and strong, so as to lift the degeneracy of the paramagetic ion. For the above purpose a symmetric, degenerate, unstable structure is taken as a cube or a square, etc. A rectilinear structure is stable even if degenerate. Jahn and Teller find :

(1) That unless the coupling between the electrons in the underlying incomplete shell of the paramagnetic ion and the immediately surrounding atoms is strong, Jahn-Teller potential will be of the 2nd order instead of the first in terms of the displacement coordinates and hence negligible, as is shown to be the case in the rare earth salts (see Van Vleck, 1939).

(2) That the Jahn-Teller distortional effect on the degenerate orbital states is of the first order compared to the effect on the spin states though it is true that, a state degenerate in spin is as unstable as the other, the conditions for attaining stability being different ;

(3) It is further shown that the indirect effect on the spins through the spin-orbit coupling is so small as to be quite masked by the vibrations associated with the zero point energy ;

(4) Lastly, that the Jahn-Teller mechanism has no effect on the two-fold Kramer's spin degeneracy.

In the above conclusions the Jahn Teller distortions of the atoms outside the closest neighbours of the paramagnetic ion are not considered, presumably on the assumption that the bond between the distant atoms and the paramagnetic ion (usually at a distance of not less than about 4 Å) is very weak. But it might be argued : (1) that though these bonds are very much weaker compared to that in the nearest cluster, in the *stable solid state characterised by internal asymmetry*, they are much larger than the thermal energy kT tending to introduce a *spherical symmetry* in the whole system, in other words tending to break down the lattice ; (2) the outer configurations of the atoms are in close contact successively with each other and ultimately with the central cluster, which is always more or less distorted in the iron group of salts at least, owing to the primary Jahn-Teller effect ; (3) the weak binding amongst the distant atoms will actually help in giving a greater distortional displacement than occursing in the nearest

cluster, as is also evident from X-ray data of the iron group of salts ; (4) thus, even if the *primary* Jahn-Teller distortion of the *distant atoms* may be smaller than that of the *nearest cluster*, the latter may cause a fairly large distortion of the distant configurations, the repercussions of which may lead to appreciable distortions in the nearest cluster, *consistent* with given conditions of equilibrium. Actually then, in considering the stabilising effect of the Jahn Teller mechanism, we should consider the entire unit cell as an asymmetric cluster about the paramagnetic ion. It will be seen that the above considerations are consistent with Van Vleck's postulate of a large indirect action of the distant atoms on the paramagnetic ion (Van Vleck *loc. cit.*), and in addition, the physical picture here lays more stress on the part played by the central paramagnetic ion in producing such action, whereas Van Vleck's picture considers the action of distant atoms as being an entirely static interaction between the atoms surrounding the paramagnetic ion.

Again, it will be seen that according to the fundamental postulates of Jahn and Teller, the self stabilising mechanism in the paramagnetic ionic cluster appears to be effective *only at short range* and appreciable only when the ground state of the ion is *orbitally degenerate*. Then, it remains to explain the following facts, namely :

(1) The appreciable Stark-splitting of the spin levels of the ground state (leaving aside the two-fold degenerate levels for odd number of electrons in the system which cannot be removed except by a magnetic field) ;

(2) The Stark-splitting of the upper degenerate orbital levels even though the lowest level in the Stark-pattern is non-degenerate.

(3) Even when the lowest level is degenerate the orbital splittings as well as the spin splittings are far too large compared to the theoretical Jahn-Teller splittings due to the distortion of the nearest cluster alone.

These indicate the obvious limitations of the original Jahn-Teller theorem and the explanations, at least qualitative, of the above follow immediately by extending the scope of the theorem to the whole crystal, as already pointed out. It has been found that for magnetically dilute solid salts containing an S-state ion or an ion, having an orbitally non-degenerate state lowest in the Stark-pattern already under a cubic field, the spin splittings, of the order of 10^{-1} to 10^{-2} cm (Van Vleck, Cr^{+++} 1930, Mn^{++} 1932, 1934), very much small compared to kT at ordinary temperatures, actually exist, which correspond to the influences of asymmetric electric fields of the nearest cluster as also the distant atoms. In other words, the Jahn-Teller *spin-distortion* is not confined to the nearest closely bound cluster alone but extends directly to the distant atoms, and perhaps to a greater extent indirectly through the intermediary of the nearest cluster. It is important to note that the above splittings are of the 2nd order compared to the spin-splittings if a primary Jahn-Teller orbital effect had

been present, *i.e.* if the lowest orbital state under a cubic field had been degenerate, *e.g.* such spin splittings would have been of the order of 1 to 10 cm^{-1} (case of V^{+++}, Ti^{+++}, etc. Van Vleck 1939) ; showing thereby that Jahn-Teller orbital effect can and does act upon the spin degeneracy through the spin-orbit coupling.

Again, if we consider the splittings of the upper orbitally degenerate levels due to asymmetric electric fields in a Stark-pattern which has a non-degenerate level lowest under the action of a cubic field, these may be attributed to Jahn-Teller effect of the nearest cluster as well as the distant atoms trying to stabilize the excited upper state. Primary Jahn-Teller splitting calculated for the upper cubic state of Cr^{+++} is of the order of 10^2 cm^{-1} to 10^3 cm^{-1} depending on the model of the field chosen (Van Vleck, 1939) though a few hundred cm^{-1} separation may also arise from the Jahn-Teller effect of the distant atoms both direct and indirect. It is noteworthy that these splittings further play an important part in deciding the resolution not only of their own spin components but of the lowest orbitally non-degenerate level, through the spin-orbit coupling (Penney and Schlapp, 1932). Again, under suitable circumstances even a small distortion of the normal spin-orbit coupling might occur causing an interaction between the excited and ground states, the so-called 'super-exchange coupling' (Van Vleck et al, 1934 ; Abragam and Pryce, 1951), which also would partially separate the spin levels, somewhat affecting the magnetic moments of the paramagnetic ion.

When, however, the case of a pattern with degenerate ground level is taken, it naturally becomes very much more complicated since the Jahn-Teller orbital distortions of the near as well as the distant atoms become very prominent and in considering the orbital and the spin splittings we have to give due consideration to all the interactions as already mentioned especially between the different orbital levels and between orbit and spin.

We shall conclude this section by making a few remarks regarding the short and the long range crystalline electric fields, rendered asymmetric by the Jahn-Teller effect as applied to the entire crystal. It is well-known that the crystalline electric fields can in general be represented by a predominent cubic part on which is superimposed a comparatively small rhombic component and by suitably adjusting the field parameters any type of symmetry may be built up. The cubic part of the field is mostly contributed by the nearest atomic cluster of paramagnetic ion and the distant atoms supply only a small part of it since this field falls off very rapidly with distance. Further, in case, the cubic field axes of the distant and the nearest groups are noncoincident, the field will only have a trigonal symmetry. The rhombic field axes of the nearest cluster, if its symmetry is purely due to *primary* Jahn-Teller distortion will coincide with those of the cubic field, and any lower symmetry than rhombic introduced either in the nearest cluster or in the unit cell as a whole must be an effect

of the *primary* Jahn-Teller distortions of the *distant atoms* and their *indirect secondary* influence on the closest cluster. In addition to this, a departure from centrosymmetry in the closest cluster might also arise owing to a mixing up of the excited and the ground states of the paramagnetic ion or from a lack of centrosymmetry in the distant atoms also. It will be seen that the fourth order rhombic fields may not always be negligible in comparison to the second order ones (Siegert, 1936, 1937 ; Van Vleck, 1930).

It is interesting to note in this connection that a purely cubic field, though sometimes postulated as a convenience (Penney and Schlapp, 1932), never arises in the solid paramagnetic salts so far studied. This would point to the fact that the removal of degeneracy of the paramagnetic ion whether in the ground state or excited state, by even a cubic field, is ultimately inseparably linked with the Jahn-Teller effect, representing the asymmetric part of the field. The separation into cubic and rhombic parts is to a large extentamathematical convenience, which has little significance in the view of the degenerate ion, whose degeneracy is removed as a whole.

3. THE VALUE OF THE STUDY OF THE TEMPERATURE VARIATION OF THE MEAN EFFECTIVE MOMENTS OF PARAMAGNETIC SALTS-TO FIND THE EFFECT OF THE DISTANT ATOMS

We have mentioned earlier the results obtained in Part I of this paper that at room temperatures for most of the magnetically dilute salts of a given paramagnetic ion except one or two, in solid state as also in solution, seem to give practically the same magnetic moments, thereby belying our expectations of getting the effect of the long range fields on the paramagnetic ion. There may be several reasons for this.

(1) Near about room temperature and higher, the mean effective moments of different salts have a greater tendency to obey the Curie law, and are less sensitive to changes of temperature. This is due to the fact that the orbital moments being largely quenched in many cases, only the spin moments are effective of which the Stark-splitting is very much smaller than kT. Hence the moments in such cases tend towards a limiting value equal to the spin only value, plus the high frequency contributions.

(2) As we have seen the contribution of the distant atoms to the cubic part of the field is much smaller than that of the nearest cluster. The major effect of the distant atoms lies in adding to the asymmetric field and in considering the mean effective moments of different salts the asymmetric effect of the field is wiped out ; only the absolute value of the cubic field and hence the moment is somewhat affected through averaged out rhombic terms.

(3) Within certain limits the Jahn-Teller effect might be a self-adjusting mechanism, and hence in passing from salt to salt, distant atoms as, also the

nearest cluster might readjust themselves such that the removal of degeneracy and hence the quenching of the moment tends to remain the same, provided the conditions of equilibrium are not exceeded. This may be particularly true for a series of solid salts of similar structure where systematic changes in the inter-atomic distances have been definitely established from X-ray data. In passing from solid to solution state, where we should expect to detect a large difference, owing to the action of the distant atoms vanishing practically altogether, and also because the self-adjusting mechanism might not be able to cope with the largely changed conditions of equilibrium, we again meet with new complications inasmuch as even the nearest cluster of atoms is in danger of being radically changed, leading to altogether different magnetic behaviours. It is therefore, frequently difficult to interpret the results in the absence of information of such structural changes.

It is evident that a study of temperature variation of the mean effective moments would lead to a much better elucidation of the Jahn-Teller mechanism as applied to the crystal as a whole, than room temperature studies, since the positions of the distant atoms and hence conditions of equilibrium would depend largely on the temperature. This we propose to discuss in the next section on the basis of the existing results.

4. DISCUSSIONS OF THE RESULTS

In the present part of the paper we shall consider the magnetic measurements of the salts of the first half of the iron group, *i e*, from Ti^{+++} to Fe^{+++} in which the tendency for the orbital quenching is greater owing to the comparatively smaller spin-orbit coupling. Fe^{++} to Cu^{++} will be treated in the next part.

The results of the experiments are given for the different salts in the form of graphs of the squares of the mean effective moments μ_{eff}^2, against absolute temperature T. In many cases graphs had to be derived from a Curie-Weiss type of relation given by the original author, so that the values plotted are already smoothed out to some extent, whereas, in several instances, such as the Leiden data and those by Jackson, it was possible to use the original experimental values which show occasional kinks and inflexions, which may not be always real. The values even of the same salt differ much from author to author so that it is always better for comparison between different salts, to take the results by the same observer wherever possible. The dearth of such data will be immediately apparent. For a full reference of the data used here Part I of this paper may be consulted (*loc. cit.*).

(1) V^{++} ion. In the two salts of V^{++} ion measured by Perrakis (1927) namely, $V_2O_2Cl_4.5H_2O$ and $VOSO_4.3\frac{1}{2}H_2O$ the mean effective moments at any temperature change slightly with time, decreasing for the first and increasing for the second salt. But the temperature variation curve (figure 2) of the freshly prepared salt in either case is parallel to that after aging,

which indicates an uncertain change in the composition or structure without, however, much change in the electric fields. Both the salts obey the Curie law approximately, apparently showing that an orbitally non-degenerate level lies lowest in the Stark-pattern of both these salts. This might be the case if the coordination of V^{+4} ion in both are tetrahedral so that the non degenerate Γ_3 level (Bose and Mitra, *l c*) is at the bottom. But then small positive spin-orbit contributions from the upper triplet Γ_4 and high frequency terms arise causing a slight variation from the Curie law with the value of the moment somewhat above the 'spin only' value. However, since the spin-orbit coupling constant λ is small in the first half of the iron group, even if the coordination of V^{+4} is octahedral so that the triply degenerate Γ_4 lies lowest, the triplet separation by the rhombic field being large compared to kT, virtually only the lowest level of the triplet contributes to the moment. Small negative spin-orbit contributions from the upper levels will be partially compensated by the high frequency terms and the Curie law will be better obeyed than in the previous case. The absolute values of the moments, however, are very different for the two salts. While the second salt has a moment close to the 'spin only' value of 3, the first salt has a much lower value even at room temperature. The diffrence in the moments observed might be due to SO_4 and Cl-ions respectively as also different number of water molecules either within or outside the closest cluster. In the absence of detailed X-ray data, it is difficult to say much about this with certainty. We have tried to fit the time-mean curves in the two cases with a formula of the type :

$$\mu^2_{eff} - 3 = A + BT + \frac{C}{T} \qquad \ldots \quad (1)$$

where A is the temperature independent spin-orbit coupling contribution from upper levels, 2nd term is the high frequency contribution and 3rd term represents mainly the spin quenching through rhombic field and spin-orbit coupling. It is found that the above constants for the two salts are respectively,

	A	B	C
$V_2O_2Cl_4.5H_2O$	-0.552	0.0001411	-62.19
$VOSO_4.3\frac{1}{2}H_2O$	-0.561	0.0015885	$+11.13$

Though much significance cannot be given to the absolute values of the above constants owing to the restricted range of temperature over which the data have been taken, it will be immediately seen from the negative and nearly equal value of the spin-orbit coupling contribution from upper levels that the crystalline fields in both the salts are nearly the same and arise from octahedral coordination of the V^{+4} ion. The high frequency terms are very small and the difference in order of magnitude is most probably owing to uncertain diamagnetic corrections applied. The real difference between the salts lies in the term C, the large negative value

in the first salt indicating a large spin quenching, which cannot be due to the crystalline electric field in V^{+4}, since the spin level has only a two fold Kramers' degeneracy. Hence, this may be due to exchange interaction leading to antiferro-magnetic quenching of the spins of the different V^{+4} ions in the unit cell. It is to be noted that the lowest spin state becomes non-degenerate due to this action and the moment of the salt tends to vanish somewhere about 25°K and it would be interesting to follow the behaviour of salt in this region. On the other hand, such a behaviour might also arise from a large negative orbital contribution, varying as inverse of T, which is possible if the field has an approximately uniaxial symmetry (Van Vleck, 1930) so that the lowest state $^3T_1$, is only separated partially (figure 1).

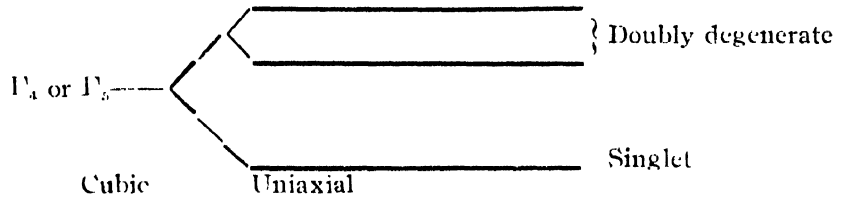

FIG. 1

Due to differences in the distant atoms in the two salts the 2nd and 4th order rhombic fields might be of comparable order and such that in one of the salts the singlet lies lowest and in the other the doublet, so that the orbital contributions of the order $1/T$ from rhombic levels are quite different. It is to be noted that in the 1st salt the curve will fall to a minimum nearabout 20°K and then rise again. The difference in the action of the crystalline electric fields, either short range or long range, is difficult to estimate in the two salts of V^{+4}. In the first of the two cases discussed above, the electric fields are not very different, whereas, in the 2nd the fields are quite different. We are studying a large number of V^{+4} salts to clarify the position.

(2) V^{+++}. The only salt for which temperature variation of the moment has been studied is the alum $VNH_4(SO_4)_2.12H_2O$ (Van den Handel Comm. Leid 249e), and it obeys Curie law fairly well down to about 14°K (figure 2). From the structure of the alums (Beevers and Lipson, 1935) it is well-known that the V^{+3} ion has six water molecules immediately surrounding it in the form of an octahedron which is so distorted as to give a trigonal field not only within the octahedron but all over the other atoms or ions in the unit cell. This would make the lowest triplet $^3T_1$ in its Stark pattern to lose only a part of its degeneracy, *i.e.*, it will split into a singlet and a doublet (figure 1). The square of the mean effective moment being not very different from the 'spin only' value of 8, throughout the temperature range studied, it appears that in this salt the 2nd order and 4th order noncubic field constants are such as to make the singlet level lowest (Van Vleck, 1939), as showin in figure 1.

This points to a special arrangement of the distant atoms and hence is an evidence for the existence of a fairly large action of long range fields in this salt. In the absence of the data on other salts of V^{+3} it is not possible to estimate the changes in the long range fields from salt to salt.

Representing the variations of μ^2_{eff} with T by a series expansion like (1) as before, we find the relation :

$$\mu^2_{eff} = 8 - 1.130 + 0.00109\,T + \frac{0.001472}{T} \qquad \ldots \quad (2)$$

to hold good down to about 14°K, showing only a fair negative contribution from the upper levels through spin orbit coupling. The two other terms are just perceptible and gives the small inclination to the straight portion of the curve seen in the graph. Below 14°K, however, the curve drops down steeply tending to zero moment at absolute zero. This occurs no doubt when the spin separation becomes comparable to kT and the lowest spin level is rendered non-degenerate.

It is not profitable to try to fit the curve below 14°K with the formula by introducing higher order terms. Without going into such complications it will be, however, seen that this steep fall in the curve would require a rather large overall separation of the spin levels of the upper limit of about 10 cm^{-1}, which is consistent with the theoretical calculations of Van Vleck (*l.c.* 1939) and of which about half is due to the action of long range fields.

(3) Cr^{+++}. Temperature variations of the salts of Cr^{+++} have been done by three schools of workers who differ amongst one another even for the same salt (figure 3). Taking first the measurements by Mlle. Serres (1932) for the salts $CrK(SO_4)_2.12H_2O$ (violet), $CrCl_3.6H_2O$ (green) and $Cr_2(SO_4)_3.16H_2O$ (violet) in the solid state, the mean effective moments are in the decreasing order and, within the moderate range of temperature studied, obey practically the Curie law. The small difference in the moments between the first and the third of the salts *if real* can be due only to differences in the distant atoms, since in both the salts the closest clusters of Cr^{+++} ions are octahedra of six water molecules. The fields are evidently stronger and more asymmetric in the first salt, orbital contributions being less. In the 2nd salt the nearest octahedron contains two chlorine ions in place of water molecules and hence both distant atoms as well as nearest atoms are different, and the asymmetry of the crystalline field is also presumably the largest, hence quenching of the moment should be the greatest, but the experimental value is actually between the two sulphates, which perhaps does not have much significance owing to the very small differences with which we are dealing. Over the entire range of temperatures down to 80°K the curves for the three salts are parallel to each other.

The Leiden measurements (208*c*, 222*e*) however, show little difference between the alum and the chloride at high temperatures, while at low temperatures below 80°K the curve for the alum tends to rise slightly whereas

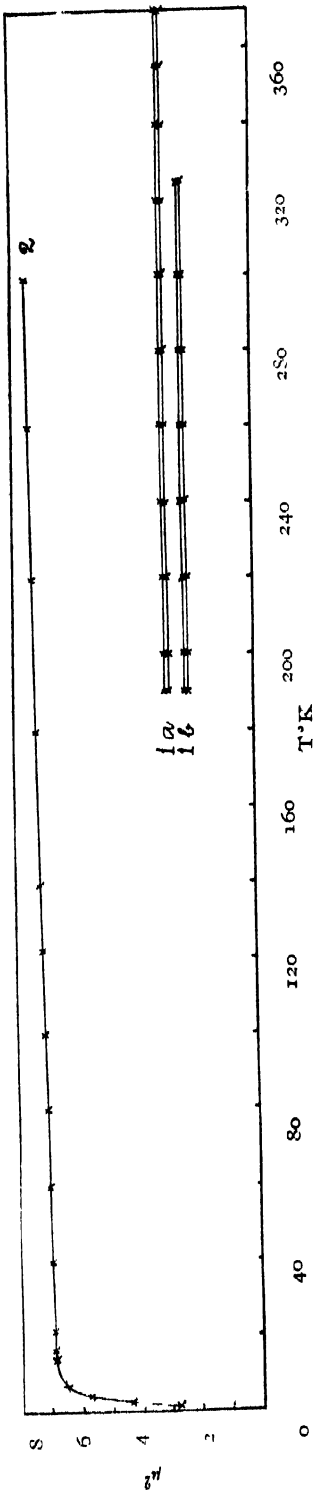

FIG. 2 (1). Perrakis (a) $VOSO_4.3\frac{1}{2}H_2O$, (b) $V_2O_2Cl_4.5H_2O$ (2). Handel and Siegert—$VNH_4(SO_4)_2.12H_2O$

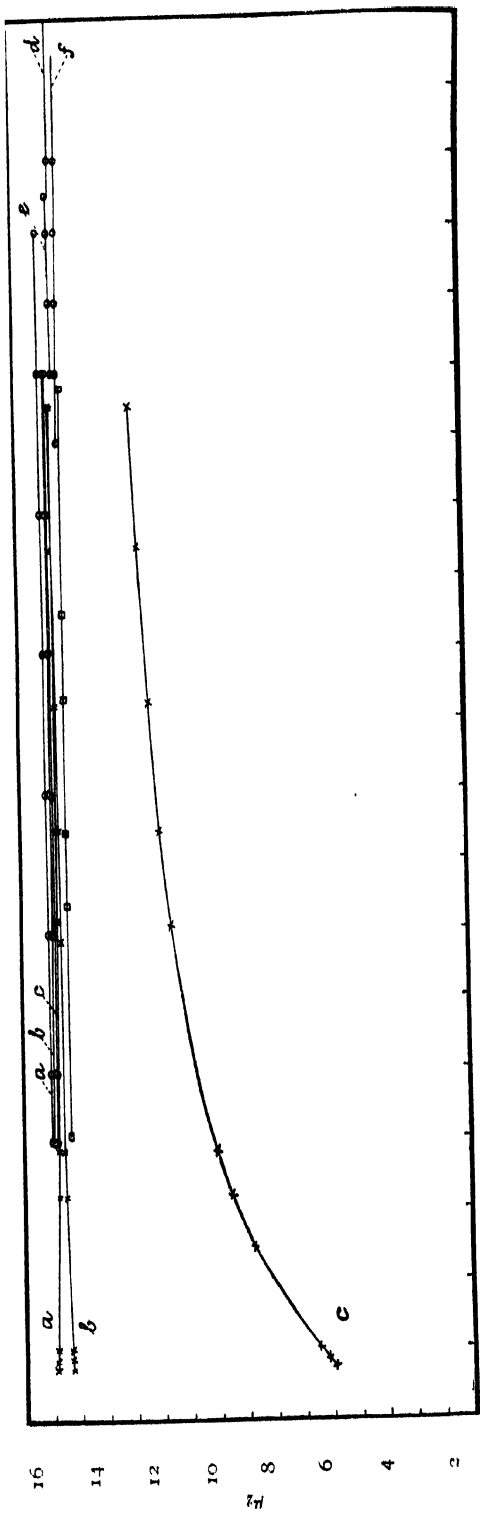

FIG. 3 (1). ×—de Haas and Gorter, (a) Cr $K(SO_4)_2$ $12H_2O$ (violet); (b) $CrCl_3$ $6H_2O$ (green) (c) $Cr_2(SO_4)_2(OH)_2$ $5H_2O$. □—Janes (2). O—Serres-(a) Cr $K(SO_4)_2$ $12H_2O$ (violet); (b) $CrCl_3$ $6H_2O$ (green); (c) Cr $(SO_4)_3.15.63H_2O$ (green); (d)-$K_3Cr(SCN)_6.4H_2O$ (3). (a)in molten state (green); (e)-(a)regealed (violet); (f)-(b)in molten state and regealed (green).

that for the chloride falls. The measurements of Serres for the molten sulphate (green) and the chloride (green) also obey Curie law approximately with a sharp decrease of the moment at the melting point which might be associated with the change in the nearest cluster as shown by the change of colour. This, however, is not supported by the further fact that on regelation the first salt retraces the same curve for the molten salt extrapolated backwards, though the colour returns to violet. The sharp change then is probably to be ascribed to the action of distant atoms becoming negligible as the lattice breaks down, since the decrease may be due to negative orbital contributions and is in the right direction. The slight difference in the slope of the curve for the green molten alum and the regealed salt has little significance as being over too restricted range of temperatures. The absolute values are all systematically higher for Serres' measurements than the Leiden workers who admit this as due to errors in their calibration.

From the above considerations it would thus appear that even in the Cr^{+++} salts where orbital Jahn-Teller effect of the nearest atoms on the ground state is negligible, the orbital effect of the excited states and the spin effect through spin-orbit coupling due to nearest atoms and those due to distant atoms may be just appreciable above the experimental errors, especially at low temperatures.

Trying to fit the experimental values into an equation of type (1) with 'spin' only value of 15 for Cr^{+++}, we find the following values for the coefficients A, B and C.

TABLE I

Salt	Author	A	B	C
$CrK(SO_4)_2\,12H_2O$	Serres	−.0615	+.0002693	—
$CrCl_3.6H_2O$	do	−.0991	−.0001363	—
$Cr_2(SO_4)_3\,16H_2O$	do	−.2309	+.0001363	—
$CrK(SO_4)_2\,12H_2O$	de Haas and Gorter	−.2595	−.0004693	1.867
$CrCl_3.6H_2O$	do	.3011	+.0001191	−4.767
$Cr_2(SO_4)_2(OH)_2.5H_2O$	do	.4.8692	+.00709	−77.38
$K_3Cr(SCN)_6.4H_2O$	Janes	−.6861	+.0000460	

The high frequency terms for the normal sulphate, double sulphate and the chloride differ very much from each other. This has not much significance bearing in mind the very small magnitude of the terms and uncertain diamagnetic correction factors. The temperature independent terms are

more important, and are all negative as they should be, and definitely point to a variation in the splitting of the cubic and rhombic orbital levels from salt to salt due both to variation of short and long range fields.

The action on the spin degeneracy is further shown by the Leiden values for the chrome alum and the green chloride which extend to much lower temperatures to about 14°K and between this temperature and 80°K the divergence in the curves for the two salts is indicated by the opposite signs of the $1/T$ dependent term. This gives us an idea of the different spin separations in the two salts orginating from different short and long range fields.

The values of the salt $K_3Cr(SCN)_6 4H_2O$ (Janes 1935) follow the Curie law very well, indicating octahedral coordination of the Cr^{+++} ion, but the absolute value is much lower than the sulphates and the chlorides, showing a large negative orbital contribution coming from upper levels through the negative spin-orbit coupling term. This is evidently more an effect of the closely coordinated SCN radicals rather than of the distant atoms.

The most interesting result, however, is shown by the basic $Cr_2(SO_4)_2(OH)_2.5H_2O$, measured in Leiden in which the moment even at room temperatures is very much below the spin only value and falls rapidly to even lower values at low temperatures. The crystalline field must be of an entirely different type here namely, due to a tetrahedral coordination of the Cr^{+++} ion, instead of octahedral as in the previous salts, so that an inversion of Stark-pattern is produced and the orbitally degenerate triplet Γ_4 lies lowest. An X-ray investigation of the structure of the salt will be welcome.

The components of the triplet are only separated comparable to kT, so that contributions from the upper rhombic levels are no longer as small nor the spins as free as in the previous cases which is shown by the large negative A and C terms. In addition to these, higher order terms do also become important at low temperature regions, as shown by small misfit with the three constant formula. Here again we cannot compare the actions of the distant atoms with the previous salts as even the arrangement of the nearest atoms is radically different. The moment in this salt tends to become zero at about 7°K much above the region of spin levels for the normal Cr^{+++} salts (of the order of about 0.1 cm^{-1}) which is perhaps justifiable in view of the stronger spin quenchings in this salt through spin orbit coupling.

In view of the fair magnetic dilution of the salt the exchange quenching of spins is not probably much important.

(4) *Cr^{++} and Mn^{+++}*. The salts of these two isoelectronic ions at room temperatures have nearly the same moment (Bose and Mitra, *l.c.*). But here the resemblance ceases and the detailed behaviour of the salts at low temperatures are very different (figure 4). The only Cr^{++} salt studied namely, $CrSO_4.6H_2O$ (Lips, 1934) with evidently an octahedral coordination about the Cr^{++} ion, obeys approximately the Curie law as is to be expected from its having the non-magnetic doublet Γ_2 at the bottom of its Stark-pattern. There is,

however, on closer observation an appreciable deviation from the spin only value of 24, as shown by the term A, as also deviations from the Curie law especially at low temperatures, given by the term C in the equation.

$$\mu_{eff} = 24 = -0.904 + .00038T - \frac{28.69}{T} \qquad \ldots \quad (3)$$

with which the experimental data fit well. These show the influence of the upper levels and also the degree of spin quenching.

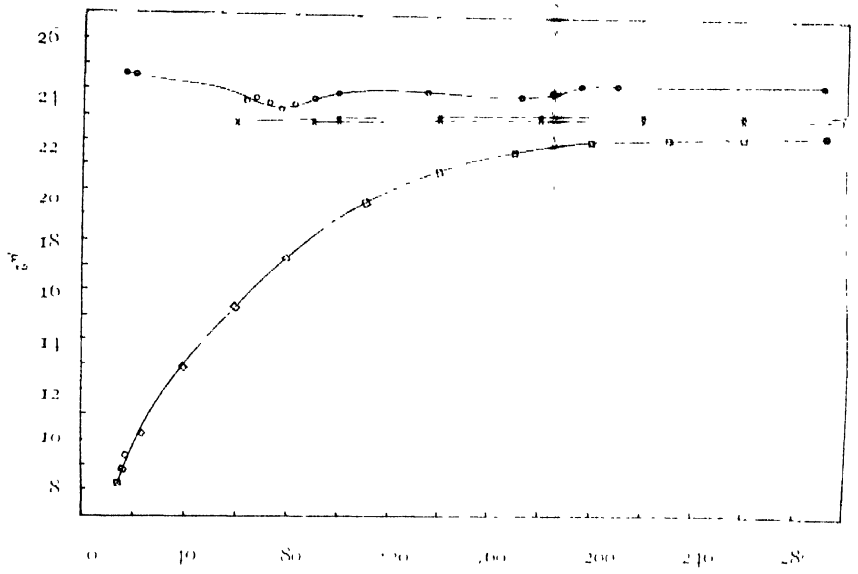

FIG. 1

1 ×—Lips, $Cr_2(SO_4)_3 6H_2O$
2 □—de Haas and Schultz, $Mn(C_2H_3O_2)_3 2H_2O$
3. O—Jackson, Manganese acetyl acetonate

The structure of the two Mn^{+++} salts studied are not known so that it is not possible to compare these with the Cr^{+++} sulphate even if we neglect the differences in their nuclear charges. The two salts Mn^{+++} acetyl acetonate (Jackson, 1935) and dihydrated acetate (de Haas and Schultz, Leid. Comm. 256) cannot, as a matter of fact, be compared even amongst themselves. An attempt to fit the data with a three constant formula gives the following :

TABLE II

Salt	Author	A	B	C
Mn^{+++} acetyl acetonate	Jackson	− 9322	+ .00420	+ .24 60
Mn^{+++} acetate dihydrate	de Haas & Schultz	− 10.9571	+ .03055	− .83.51

Conformity with formula in either case is only approximate, indicating the necessity for introducing high order terms. However, without attempting this complication, we see that a large temperature independent term, about eleven times larger than in the acetyl acetonate, obtains in the acetate, no doubt due to much stronger fields in the latter. The *B* and *C* terms are also very much different the latter being even opposite in sign for the same reason. It is of course possible that the coordinations in the two salts might be octahedral and square respectively so that a much greater quenching without a change in the sign of either *A* or *B* terms, occurs in the latter salt. This is borne out further by the fact that the *A* term in acetyl acetonate has a comparable value to that of the $CrSO_4.6H_2O$. That covalency plays a large part in quenching the spins in the case of the acetate is well known from the recent results on the other acetates of the iron group (Mookherji, 1945, Guha, 1951). Very recently, however, Bleaney and others (1952) have invoked "antiferromagnetism" in copper acetate, with orbital Stark pattern exactly similar to the Mn^{++} salt, but with only a twofold Kramer's spin degeneracy in the former, in order to explain its tendency to become nonmagnetic at liquid hydrogen temperatures. No doubt such a quenching effect of the exchange interaction would be adequate to explain the behaviour in copper acetate with the twofold Kramers degeneracy which crystalline fields cannot remove, and also presumably in the other acetates but then the large temperature variation of the moments and the strong anisotropy of the single crystals of the acetates (Mookherji *l.c.*) are difficult to understand.

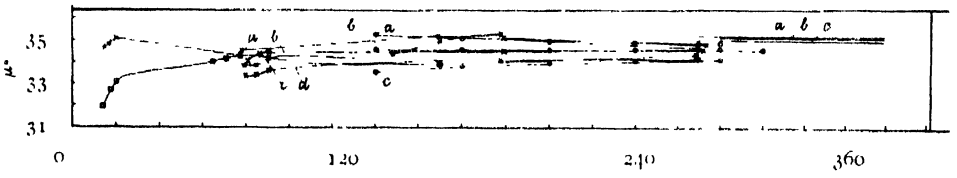

FIG. 5

1. × Jackson,
   (a) $Mn(NH_4SO_4)_2\,6\,H_2O$ (b) $Mn(NH_4SO_4)_2.6H_2O$, (c) $MnSO_4.5H_2O$, (d) $MnSO_4.4H_2O$.
2. □ Onnes & Oosterhuis,
3. ○ Lallemand
   (a) $MnCl_2\,5\,H_2O$.
   (b) $MnCl_2\,4\,H_2O$ (solid) and aq solution
   (c) $Mn_2P_2O_7$
4. Bose, aqueous solutions (conc. in gms/gm. soln,
   (a) $MnSO_4$, c=.2773, .3755, $Mn(NO_3)_2$ c=.4334, $MnCl_2$, c = 2784. (b) $MnSO_4$, c=.3241, $Mn(NO_3)_2$, c=.5690, (c) $Mn(NO_3)_2$, c=.5948, $MnCl_2$, c=.3671.

It would appear from the results that the acetyl acetonate is not so covalent as the acetate, which is not surprising in view of the larger dimensions of the former molecule.

(5) Mn^{++} and Fe^{++} salts ; have been very widely studied for a large number of salts in solid and solution states (figures 5 and 6). In these two

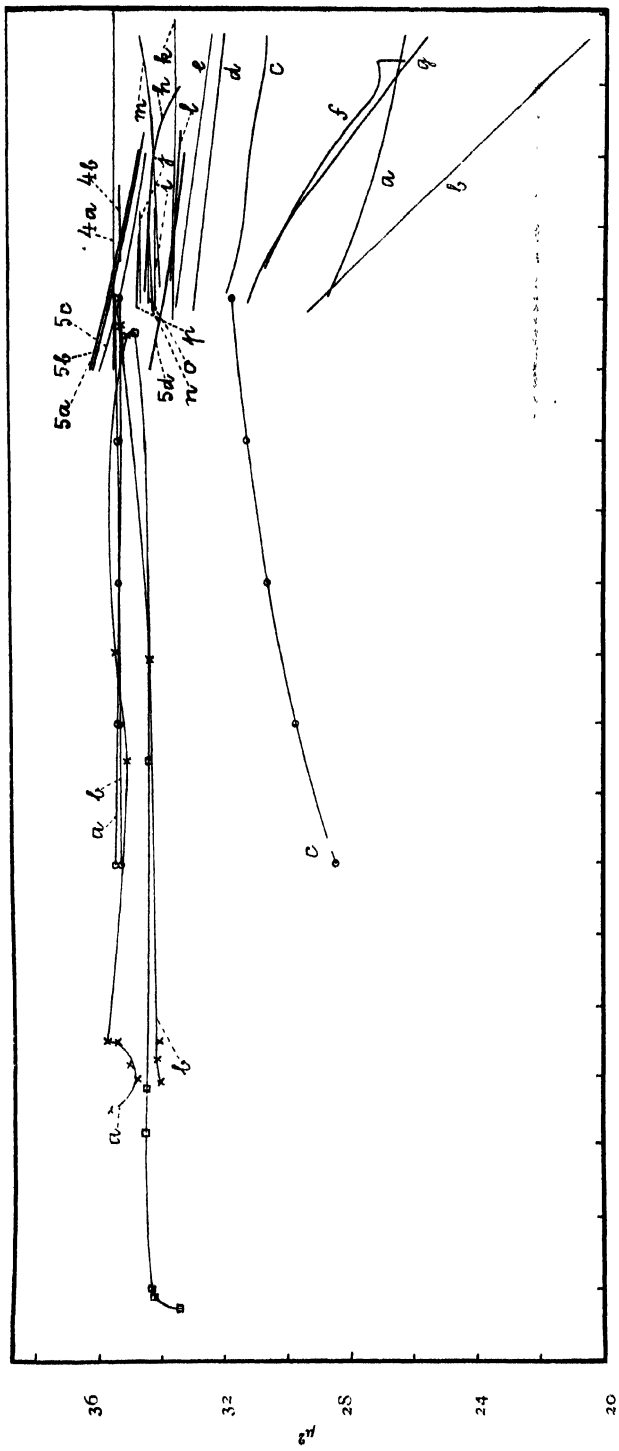

FIG. 6

1. ×—Jackson. (a) Potassium ferri-oxalate (b) Ferric acetyl acetone.
2. □—Onnes & Oosterhuis. $Fe\,NH_4(SO_4)_2\,12H_2O$.
3. ○—Lallemand, (a) $Fe(NO_3)_3\,9H_2O$ (b) $Fe\,Cl_3.6H_2O$, (c) $Fe\,Cl_3.2NH_4\,Cl.H_2O$
4. Lallemand, aqueous soln (a) $Fe\,Cl_3$ (b) $Fe\,Cl_3.2NH_4Cl$
5. Fahlenberach, aq. soln of $Fe\,cl_3$ (a) c=6 60 gms/100 c.c. soln. (b) c=1 98 gms/100 c.c. soln. (c) c=0 829 gms/100 c.c soln. (d) c=0.348 gms/100 c.c Soln.
6. Bose, aq. soln. conc. c in gms/gm. soln. $Fe_2(SO_4)_3$. (a) .3392, (b) .2548, (c) .2694, (d) .1619, (e) .1103; $Fe(NO_3)_3$, (f) .3728, (g) .1832. (h) .3072, (i) 1807, (j) .0865; $Fe\,Cl_3$, (k) .4428, (l) .1985, (m) .3319 (n) .2903, (o) .1922, (p .0937

ions where there are no orbital contributions to be considered, Van Vleck and Penney (1934) have shown that the mean moment should obey a Curie law up to and inclusive of the terms in $1/T$. The deviations from Curie law of a given salt, and from salt to salt, if existing should thus be of an even higher order. This is also as demanded by Jahn-Teller condition of stability as applied to spins, discussed in an earlier section.

Excepting $Mn_2P_2O_7$, of which the structure is not known, all the other salts studied namely, $Mn(NH_4SO_4)_2.6H_2O$, $MnSO_4.5H_2O$, $MnSO_4,4H_2O$, $MnCl_2.5H_2O$ and $MnCl_2\,4H_2O$ have presumably similar octahedral coordination of the Mn^{++} ion. Taking the measurements of Jackson (1923, 1924, 1927) and Onnes and Oosterhuis (Leid. Comm. 132c) for the first three salts, peculiar kinks and bends in the curves appear at certain temperatures, possibly owing to some change in the composition of the salts. There is, however, no doubt that there are appreciable differences in the values especially at low temperatures in these salts, which are evidently partly due to changes in the long range fields, quenching of the moments being the least for the double sulphate and greatest for the tetrahydrate. At liquid hydrogen temperatures rapid fall in the moment is found to occur for the double sulphate as also the tetrahydrated sulphate, no doubt due to appreciable depopulation of the upper spin levels and exchange or super-exchange interactions might also become more important. Similar results are also obtained by Lallemand (1935) for the pentahydrated and tetrahydrated chlorides.

There is further evidence of an appreciable Jahn-Teller spin effect of the distant atoms from the measurements of the solutions of $MnSO_4$, $MnCl_2$ and $Mn(NO_3)_2$ (Bose, 1935) which shows practically the same values of the moments at different temperatures and concentrations, very nearly equal to spin only value of 35 and *definitely above those of the solid salts*, as they should be, in the absence of long range fields in solution. When we consider the ferric salts, however, we find no appreciable difference between the salts $FeCl_3.6H_2O$ and $Fe(NO_3)_3.9H_2O$ done by Lallemand (1935), which obey practically the Curie law with spin only value of the moment. This might indicate a difference in structure in the two salts, compensating the difference in long range field actions from Cl^- and $(NO_3)^-$ respectively. Same holds true also for the ferric alum done at Leiden (Onnes and Oosterhuis, Leid. Comm. 139e), only the absolute value of the moment is much lower, but it is not safe to draw any conclusions from these results in view of the smallness of the effect we are seeking. However, a steep fall in the Leiden curve at hydrogen temperatures reminds one of the similar behaviour in Mn^{++} salts. Ferric acetyl acetone (Jackson, 1933) shows a small deviation from Curie law at high temperatures and a downward bend at liquid oxygen temperature which perhaps is a precursor of a minimum in the curve in this region. This is actually shown quite clearly in the curve for ferric potassium oxalate (Jackson, 1933), which again has a larger absolute moment

than the previous salt all along its course and shows one more maximum and minimum in the higher temperature region. These facts are rather difficult to reconcile with the spin only ground state of the ferric ion unless we postulate some sort of violent changes in the crystalline fields.

Most surprising behaviour is, however, shown by Lallemand's (*l.c.*) data on $FeCl_3$, $NH_4Cl.H_2O$ which in the solid state has a very low moment and the moment falls fairly rapidly to even lower values, indicating strong anti-parallel coupling of at least some of the spins, either due to covalency or exchange interaction. It is very interesting to note that in the state of solutions the moment immediately goes back to normal spin only value and Curie law is followed. It is difficult to judge the action of distant atoms in ferric salts from a comparison of values in solid state and solutions since strong hydrolysis, with perhaps ferromagnetic group formations, sets in the aqueous solutions of these salts. But preventing hydrolysis by adding suitable acids Bose, (1935) and Lallemand (1935) have shown that the solutions of the sulphate, chloride and nitrate tend to approximate conformation of spin only limiting values and Curie law, as the action of the distant atoms vanish.

It appears that in Fe^{+++} and Mn^{++} salts, though here the ions are in a spin state, the effect of the distant atoms is more prominent than in the Cr^{+++} salts where orbital contributions are not negligible. This is evidently due to the much larger absolute moments in the former salts. It will be seen that in general, in all these cases the effect of the long range cubic fields are more important at higher temperatures and remain more or less constant down to the lowest temperatures, whereas, the asymmetric fields rise to importance only at sufficiently low temperatures.

CONCLUSIONS

From the foregoing discussions it appears that in the first half of the iron group the ions, irrespective of whether the lowest level in the Stark-pattern is orbitally degenerate or not, have at best only feeble orbital moments and hence their effective moments approximate to spin only values and obey nearly the Curie law. The differences in the action of short range and long range fields are, however, definitely noticeable, in the salts of most of the ions on proceeding to a higher order approximation of the behaviours of the different salts particularly at low temperature regions, wherever sufficient reliable data are available.

The latter half of the iron group with much greater orbital contributions to their moments would be more sensitive to changes in both short and long range fields and we proceed to discuss these in the next part of the paper.

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